

MAY 15 2008

Application No. 10/516,295
Amendment dated May 15, 2008
Reply to Office Action of February 15, 2008

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REMARKS

Claims 1-4 and 7-10 are now pending in this application. Claim 1 has been amended to recite a unit for molecular weight (g/mol).

The amendment does not present new matter or raise new issues. In view of the preceding amendments and the following remarks, the applicants respectfully request reconsideration of the above-identified application.

THE CLAIMED INVENTION

In brief, the amended claims cover a curable composition resulting from a Michael reaction, which can be crosslinked at low temperatures or room temperature, but is also storage stable at room temperature, and does not suffer from the drawbacks of strong basic catalysts (which may impart yellowing cloudiness) or hydrolysis instability to the coating. In particular, the claimed invention requires a **tertiary alkyl phosphine** as the basic catalyst in a **general** Michael reaction of claimed compounds (A) and (B). Compound (A) has at least two unsaturated groups which are activated for Michael addition, and compound (B) has at least two activated hydrogen atoms.

Furthermore, the claimed invention requires a carboxylic acid (D) in the curable composition to be a saturated fatty acid having a molecular weight 80 g/mol or less, and the carboxylic acid (D) to be added before the tertiary alkyl phosphine (C).

OBJECTIONS

In the Office Action, it was incorrectly noted that the Information Disclosure Statement ("IDS") of August 21, 2007, failed to include a copy of the cited reference.

In fact, a copy of the reference was included with the IDS of April 26, 2007. A copy is also attached to this Response.

In the Office Action, claims 1-4 and 7-10 were objected to for informalities.

In light of the Examiner's suggestion, claim 1 has been amended to recite "molecular weight

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of 80 g/mol or less.” Accordingly, the applicants respectfully request reconsideration and withdrawal of this objection.

REJECTIONS – 35 U.S.C. §103

In the Office Action, claims 1-4 were rejected under 35 U.S.C. §103(a) as being unpatentable over U.S. Patent No. 5,959,028 to Irie, et al., in view of U.S. Patent No. 5,268,473 to Moren, et al., and U.S. Patent No. 5,219,958 to Noomen, et al.

The applicants respectfully traverse this rejection.

The rejection of claims 1-4 were based on the combination of Irie, Moren, and Noomen. Irie was cited for the disclosure of a Michael reaction of claimed components (A) and (B); Moren was cited for the disclosure of tertiary phosphine catalyst used in a Michael reaction; and, Noomen was cited for the disclosure of blocking a Michael reaction catalyst with carboxylic acid.

The combination of the references fail to arrive at the claimed invention because Moren teaches a very specific type of Michael reaction involving azlactones, which does not apply generally to all Michael reactions, and certainly not to the claimed Michael reaction of components (A) and (B) which do not involve any azlactones. That is, Moren’s disclosure of tertiary alkyl phosphine as a Michael addition catalyst does not apply to the claimed Michael addition because Moren is only directed to a very specific Michael reaction of azlactones. Given Moren’s narrow teaching of Michael reaction catalysts, no motivation exists to supplement Irie with Moren.

In particular, Moren discloses that a Michael reaction of azlactones and carbon acid produces a specific kind of Michael adducts which contain a stronger base than a phosphine catalyst. In fact, Moren teaches that the Michael adducts may function as the actual catalytic agent, rather than the tertiary alkyl phosphine:

Generally, it is advantageous to employ a catalyst, and the most efficient catalysts are bicyclic amidines and trivalent phosphorus compounds described in U.S. Pat. No. 4,874,822 which is incorporated herein by reference . . . [The reaction] involves initial Michael addition of the catalysts to the 2-alkenyl azlactone. In contrast to the Michael donors of the

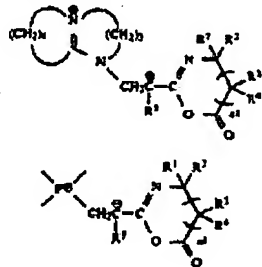
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present invention, these catalysts possess no readily exchangeable proton. Consequently, charged or so-called "zwitterions" structures such as IXa and IXb are formed:



[The] Michael adducts contain a stabilized carbanion which is a stronger base than either amidine or phosphine catalyst. The zwitterionic intermediate thus formed in situ may be the actual catalytic agent responsible for forming the enolate ion.

(Moren, col. 12, ln. 45-col. 13, ln. 23). That is, **Moren** involves a Michael addition of the catalyst and a 2-alkenyl azlactone, which forms a very specific structure, zwitterion, which itself contains a base that serves as the catalytic agent in forming the enolate ion.

Furthermore, **Rasmussen** (U.S. Patent No. 4,874,822 – the reference incorporated by reference in **Moren**) makes an even narrower disclosure that trivalent phosphorus compounds used as a Michael addition catalyst is effective only for alkenyl azlactones, but not for saturated azlactones:

The unusual effectiveness of the catalysts of the present process is not well understood. The fact that both stronger and weaker bases are less effective as catalysts indicates that factors other than base strength must be important. Also, whereas U.S. Ser. No. 910,528 teaches that bicyclic amidines such as DBU and DBN are quite effective catalysts for the reaction of alcohols with saturated azlactones, it was completely unexpected that these same catalysts would be an order of magnitude more effective (i.e. greater than ten times the reaction rate) for reactions with alkenyl azlactones. Even more surprising is the fact that the trivalent phosphorus catalysts are ineffective for catalysis of alcohol/saturated azlactone reactions.

(Rasmussen, col. 6, lns. 19-33).

In other words, **Moren's** teaching of trivalent phosphorus compounds is narrowly tailored for azlactone Michael additions, and **Rasmussen** discloses that, even for azlactone reactions,

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trivalent phosphorus compounds are effective catalysts only for a particular kind of azlactones.

Neither Irie nor Noomen makes any mention of Michael reactions and azlactones. Irie simply teaches a Michael reaction between "(a) a component having a plurality of α,β -unsaturated carbonyl groups and (b) a component having a plurality of activated methylene group." (Irie, Abstract). The reference makes no mention of azlactones or zwitterionic intermediates. Therefore, no motivation exists to import Moren's specific and narrow teachings to Irie or Noomen.

Accordingly, the cited references fail to disclose the tertiary alkyl phosphine catalyst (C) of the claimed invention which is used in a Michael reaction of claimed compound (A), having at least two unsaturated groups which are activated for Michael addition, and claimed compound (B), having at least two activated hydrogen atoms.

Furthermore, as to the claimed combination of tertiary alkyl phosphine (C) and carboxylic acid (D), which is a saturated fatty acid having a molecular weight of 80 g/mol or less, the Examples in the Specification clearly show unexpected improvements in terms of compositions which can be crosslinked at low temperatures and, at the same time, remain stable at room temperature.

Furthermore, the use of tertiary alkyl phosphine (C) and carboxylic acid (D) in the claimed Michael reaction provides compositions which do not suffer from the drawbacks of strong basic catalysts, which may impart yellowing, cloudiness, and hydrolysis instability to the coating. Tables 1 and 2, below, show that the claimed compositions exhibited unexpected improvements in terms of solvent resistance, pencil hardness of the cured coatings, and storage stability.

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Table 1:

Example	Tertiary alkyl phosphine (C)	Carboxylic acid (D)	Solvent resist./ Pencil hardness ¹ (25°C/ 7 days)	Solvent resist./ Pencil hardness ² (80°C/ 30 min)	Solvent resist./ Pencil hardness ³ (160°C/ 20 min)	Storage stability at Room Temp.
1	TOP	Formic acid	25	25	25	> 6 months
2	CCP	Acetic acid	25	25	25	1 month
3	TOP	Malonic acid	no cure	25	25	> 6 months
4	TOP	Acetic acid	15	15	5-25	3 months
5	CCP	Malonic acid	no cure	25	25	6 months
6	CCP	Formic acid	35	40	5-25	> 6 months
7	TOP	Glyoxylic acid	no cure	25	25	1 month

Table 2:

Example	Tertiary alkyl phosphine (C)	Carboxylic acid (D)	Solvent resist./ Pencil hardness ¹ (100°C/30 min)	Solvent resist./ Pencil hardness ² (140°C/20 min)	Storage stability at Room Temp.
9	TOP	Formic acid	25	25	6 months
10	TOP	Acetic acid	25	25	4 months
11	TOP	Malonic acid	25	25	6 months
12	TOP	Glyoxylic acid	25	25	3 months

(Tables 1 and 2, Specification, p. 20, 22).

In summary, the cited references fail to disclose the claimed Michael reaction which uses a tertiary alkyl phosphine catalyst for reacting claimed components (A) and (B) – rather than only limited to azlactones as taught in **Moren**. In addition, the Examples support unexpected improvements in combining tertiary alkyl phosphine (C) and a carboxylic acid (D) in a Michael reaction. For the foregoing reasons, the applicants respectfully submit that **Moren**, **Irie**, and **Noomen** fail to render obvious the invention recited in claims 1-4, and request reconsideration and withdrawal of this rejection.

In the Office Action, claims 7-10 were rejected under 35 U.S.C. §103(a) as being unpatentable over **Irie**, in view of **Moren** and **Noomen**.

For the same reasons discussed above, **Moren** and **Noomen** fail to render obvious the invention recited in claims 7-10. Therefore, the applicants respectfully request reconsideration and withdrawal of this rejection.

In the Office Action, claims 1-4 and 7-10 under 35 U.S.C. §103(a) as being

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unpatentable over U.S. Patent No. 6,897,264 to Lachowicz, in view of Noomen.

Lachowicz fails as prior art against the claimed invention. The instant application's effective filing date of June 14, 2002 (priority application EP 02013480.5), precedes the U.S. filing date of Lachowicz, December 18, 2002. A certified copy of the priority application is on record.

Noomen alone fails to render the claimed invention obvious.

Accordingly, the applicants respectfully request that this rejection be reconsidered and withdrawn.

REJECTIONS -
NONSTATUTORY NONOBVIOUSNESS-TYPE DOUBLE PATENTING

In the Office Action, the following rejections were based on nonstatutory nonobviousness-type double patenting:

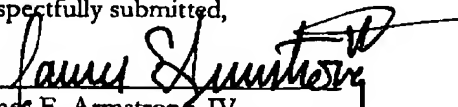
- Claim 1 as being unpatentable over claim 1 of Lachowicz, in view of Brindöpke, et al, and in view of Noomen;
- Claims 2-4 and 7-10 as being unpatentable over claim 1 of Lachowicz, in view of Brindöpke, Noomen, and Irie.

In order to overcome this rejection, the applicants enclose a terminal disclaimer over Lachowicz.

In view of the above amendment and terminal disclaimer, the applicants believe the pending application is in condition for allowance.

Dated: May 15, 2008

Respectfully submitted,

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Encls: Terminal Disclaimer & copy of Assignment (5 pages)

Clemens, R.J. et al. "A Comparison of Catalysts..." (9 pages)

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A Comparison of Catalysts for Crosslinking Acetoacetylated Resins via the Michael Reaction

Robert J. Clemens and F. Del Rector
Eastman Chemical Products, Inc.*

Thermoset coatings can be prepared at ambient temperatures from acetoacetylated resins, polyacrylates or unsaturated resins, and a basic catalyst, via the Michael Reaction. A model of this crosslinking system, the reaction of isobutyl acetoacetate and ethyl acrylate, was carefully studied to determine the effects of different catalysts. Several acetoacetylated resins were crosslinked via the Michael reaction and the physical properties of the resulting thermoset coatings were evaluated.

INTRODUCTION

The coatings industry is continually searching for new methods of preparing thermoset polymers at ambient temperatures, and several research groups have recently examined acetoacetylated polymers in this regard. Acetoacetyl groups are amphoteric, and thus can participate in a variety of chemical transformations which might be used to modify or crosslink polymers (Figure 1).¹ Reagents which are known to react readily with acetoacetyl groups include amines, which react with the acetoacetyl carbonyl group; aldehydes, which react with the active methylene group; and metal ions, which chelate with the enolate anion formed by treatment of the acetoacetyl group with a base. Each of these latter methods has been used to functionalize or crosslink acetoacetylated poly-

mers at ambient temperatures. The active methylene group of the acetoacetyl functionality is also known to participate in the Michael reaction, providing yet another approach for ambient temperature crosslinking.

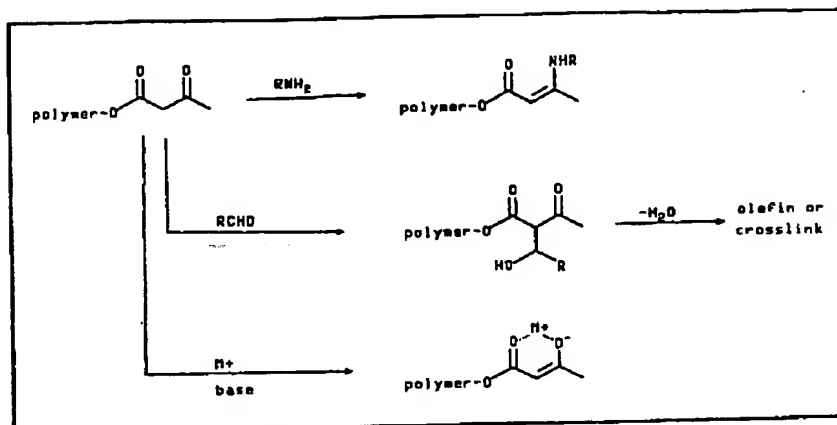
The Michael reaction (Figure 2) is the base-catalyzed addition of a carbanion (the Michael donor) to an activated olefin (the Michael acceptor) such as an acrylate ester.² While the Michael reaction of acetoacetylated polymers was described as early as 1956,³ it has only recently become of interest in thermosetting coatings systems. Technology has been described for crosslinking butyl acrylate/acetoacetoxyethyl methacrylate (AAEM) copolymers with polyacrylates such as trimethylolpropane triacrylate (TMPTA) in the presence of a strongly basic catalyst at ambient temperatures.⁴ The possibility of preparing high-solids coatings based on low molecular weight acetoacetate esters of simple polyols or polyester resins is intriguing. Preliminary experiments in this latter area, although promising, revealed a dramatic variation in cure rates of different systems. We therefore sought a greater general understanding of this Michael crosslinking technology, with a special emphasis on the catalysts; our efforts in this regard are the subject of this paper.

The Michael reaction is well documented in a qualitative sense for small molecules, but virtually all kinetic studies on the Michael reaction have been run with general base catalysis in buffer solutions, rather than with catalytic quantities of base in organic solvents.⁵ This lack of background information, coupled with the inherent difficulties of evaluating the formation of thermoset coatings on a molecular level, led us to study a model system. Our model system provided us with a greater understanding of the crosslinking process which is effected via the Michael reaction and also facilitated the evaluation of new catalysts.

*Presented at the Water-Borne and Higher-Solids Coatings Symposium, in New Orleans, LA, on February 1, 1988.
*Kingsport, Tennessee and Eastman Chemicals Division Research Laboratories, Eastman Kodak Co., New Haven, CT 06502.

R.J. CLEMENS and F.D. RECTOR

Figure 1—Acetoacetyl groups

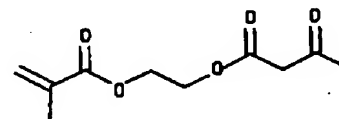


THE MODEL SYSTEM

Isobutyl acetoacetate [(1) in Figure 3] was selected to model an acetoacetylated polyester derived from neopentyl glycol or cyclohexanedimethanol, and ethyl acrylate [(2) in Figure 3] was used to model the TMPTA. Compounds 1 and 2 were dissolved in n-butanol (nBuOH), tetrahydrofuran (THF), or xylene, at concentrations which approximated the concentrations (1 M) of the two functional groups in a high solids coatings system; the resulting solutions were carefully equilibrated at 25°C (77°F). A catalyst was added to each solution, and aliquots were periodically withdrawn, neutralized, and analyzed by gas chromatography (see Experimental section for further details). In sample runs with 5 mole% (relative to acetoacetyl groups) of benzyltrimethyl ammonium methoxide or KOH as the catalyst, the formation of both a mono (3) and a bis-Michael adduct (4) was observed (Figure 3). The reaction proceeded until virtually all of the ethyl acrylate was consumed (Figure 4).

Analysis of the data from a series of model reactions suggested that the rate of the Michael reaction had a first order dependency on the acrylate concentration, but was independent of the concentration of the isobutyl acetoacetate (1). Indeed, the rate of reaction was unchanged when the acetoacetate concentration was reduced ten-fold. This data is consistent with a reaction mechanism in which the deprotonation of the acetoacetate ester is rapid and af-

fords a steady-state concentration of the reactive enolate anion (5) (Figure 5). The model reaction is more complex than might be surmised from the apparent first order nature of the process since, after the reaction has started, there are two acetoacetate anions [(5) and (7)] competing for the ethyl acrylate. From a coatings development standpoint, however, the rate of Michael reaction of ethyl acrylate is the critical factor; each molecule of ethyl acrylate consumed in the model system corresponds to the formation of a branch point or a crosslink in an actual resin formulation. A more detailed picture of the overall mechanism is presented in Figure 5;* several acid-base equilibria, particularly anion protonation by the solvent or other acetoacetate species, have been omitted for clarity.



AAEM

Our model system showed the rate-limiting step of the Michael reaction to be dependent upon the acrylate (1)

*Our simplified, pseudo-first-order analysis made no effort to determine the contribution of 1,5, the rate of reaction of the mono-Michael adduct anion (7), to the absolute rate. It appeared to be small during the early phases of the reaction in which coatings behavior was simulated.

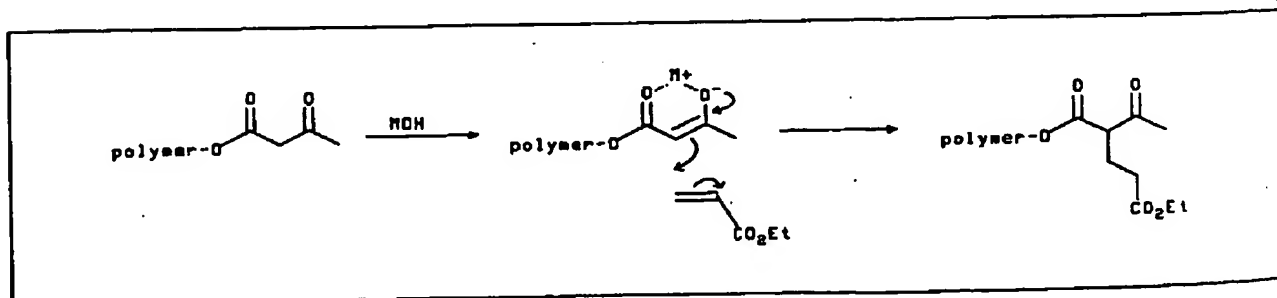


Figure 2—Michael reaction

CROSSLINKING ACETOACETYLATED RESINS

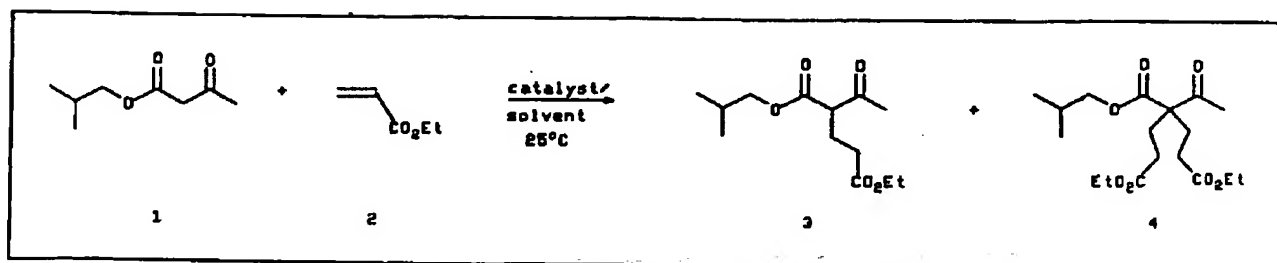


Figure 3—Formation of both a mono (3) and a bis-Michael adduct (4) as a result of sample runs with 5 mole% (relative to acetoacetyl groups) of benzyltrimethyl ammonium methoxide or KOH as the catalyst

and acetoacetate anion (5) concentrations. In coatings systems, adjustment of the acrylate concentration would be limited by stoichiometric considerations and could not be used to control the rate of crosslinking. The dependence of the reaction rate on the acetoacetate anion concentration, however, was quite promising since the concentration of this anion could be varied by both the amount of catalyst which was used and by the initial deprotonation equilibrium (k_1/k_{-1}). We therefore planned to examine the effect of a variety of bases on this deprotonation equilibrium via our model system.

The appearance of a bis-Michael adduct in our model reactions was relevant to subsequent work; it greatly complicated kinetic analysis of the model system and implied that less than an equivalent of the acetoacetate functionality was required relative to the acrylate. More importantly, coatings formulations in which large amounts of the bis-Michael adducts were formed would be expected to cure faster and to gel sooner than those in which only mono-Michael adducts were produced. The Carothers equation was used to predict the extent of reaction necessary to achieve infinite molecular weight as a function of the number of reactive functional groups which were present on the resin and on the crosslinking reagent.⁶ This latter information is important when considering the pot life of various systems (note that a bifunctional crosslinking reagent would be expected to provide a much longer pot life than a tetrafunctional one for a given catalyst system). A graphical rendition of the Carothers equation (Figure 6) was used to predict the extent of reaction for which our model system might be expected to approximate the solution chemistry in actual coatings systems.⁸

EVALUATION OF CATALYSTS

It is known that Michael reactions between acetoacetyl esters and acrylates occur readily at 25°C with strong bases such as methoxide and hydroxide, but not with weaker organic bases such as triethylamine.¹ This can be explained by the position of the deprotonation equilibrium (k_1/k_{-1}), in which weaker bases afford lower steady-

state concentrations of the anion. We selected commercially available amidine and guanidine bases (Table 1) which had pK_b values intermediate between hydroxide and triethylamine for our studies. The active methylene protons on acetoacetate esters have a pK_a of ~ 12 , and the methine proton of the mono-Michael adduct (3) has a pK_a of ~ 13 , so these bases were expected to vary the deprotonation equilibria and, consequently, the relative concentration of the acetoacetate anion. It was expected that the hydroxide bases would rapidly deprotonate the acetoacetate ($k_1 \gg k_{-1}$ or k_2) and thus establish a limiting velocity for the Michael reaction under the conditions of our model system. This limiting rate appeared to be $30 \times 10^{-5} \text{ sec}^{-1}$ (Figure 7).*

As shown in Figure 8, TMG was found to be an effective catalyst for the Michael reaction of our model system, and was also found to be less sensitive to the reaction solvent than KOH. It also catalyzed the Michael reaction less effectively, as was predicted.

The relative reaction rates which resulted from using the various bases in our model system are shown in Table 2, and the effect of various catalyst concentrations on the rate is shown in Table 3 and Figure 9. Rate constants over

*The reaction rates are presented as pseudo-first-order rate constants, as determined from the slope of a plot of $\log [EA]$ vs time, as derived from the integration of the rate expression $d[EA]/dt = -k_{\text{obs}}[EA]$, where k_{obs} is a function of the concentration of the base (held constant), the deprotonation equilibrium (constant for a given base), and the rate constants k_2 and k_3 (at later stages of the reaction). Qualitative observations suggest $k_3 > k_2$, but the impact of this second process is only seen later in the reaction as [3] builds up, and is lessened by the higher pK_a of the methine proton of 3. A rigorous study of our model system would require separating k_2 and k_3 , but would have provided little additional information to our coatings application.

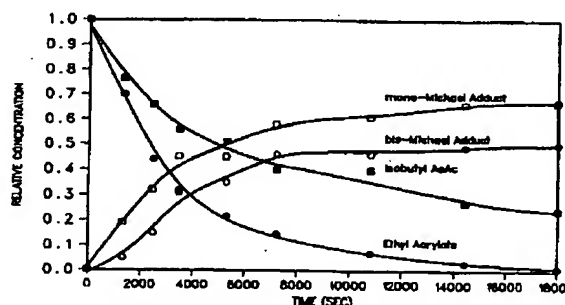


Figure 4—Michael reaction of the model system; KOH catalyst (5 mole%); 25°C

*The model study is the assumption that the model system reflects the kinetics of actual coatings systems.

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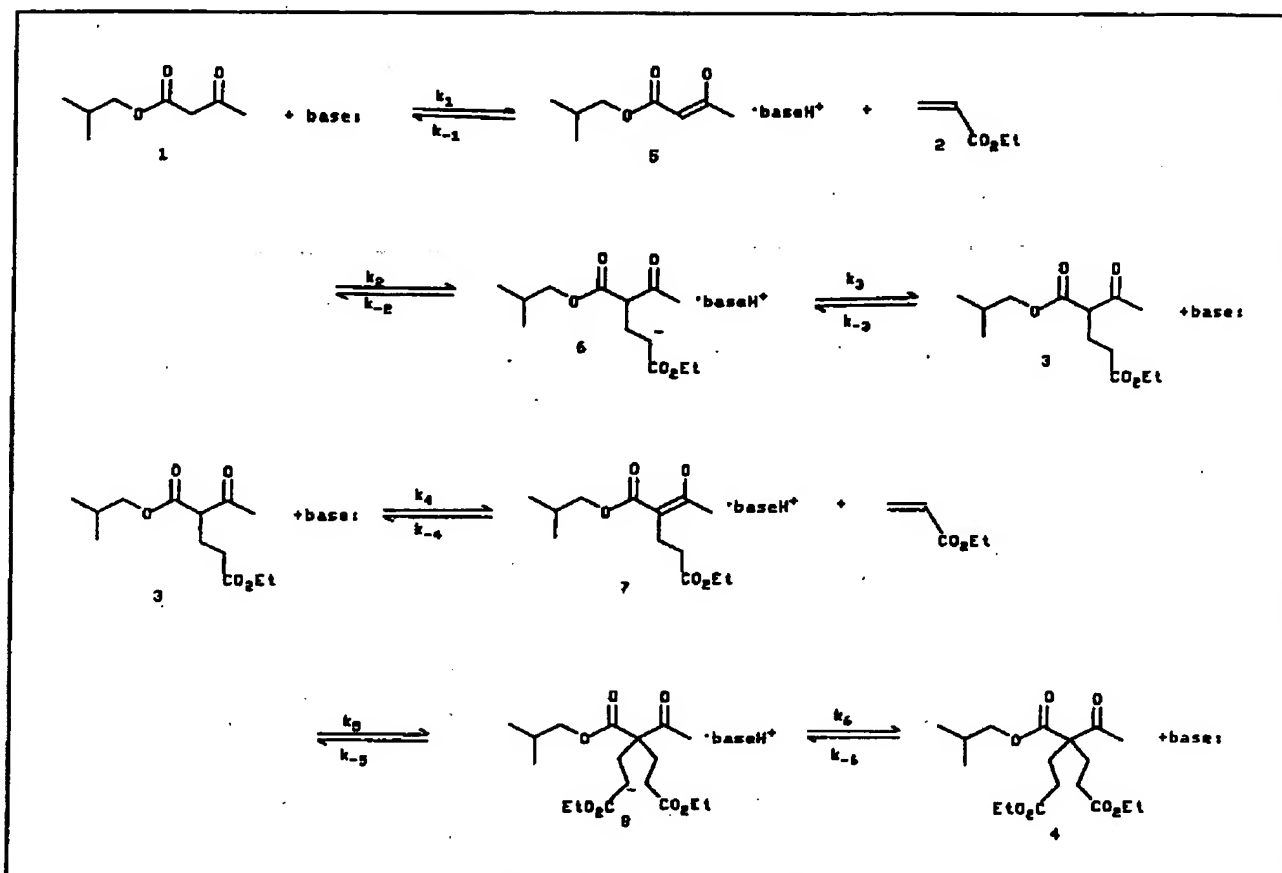


Figure 5—Overall reaction mechanism

$20 \times 10^{-5} \text{ sec}^{-1}$ in our model system usually correlated with extremely short pot lives in actual coatings systems, while rate constants less than $2 \times 10^{-5} \text{ sec}^{-1}$ could not be expected to provide effective cure in a coating.

The results in Table 3 show that amidine and guanidine bases are clearly effective catalysts for the Michael reac-

tion;⁷ TMG and DBU provided the lower reaction rates which were expected as k_{-1} became larger relative to k_1 . The rate of reaction achieved with the DBN was unexpected and is not yet fully understood; possibly the pK_b of DBN in our system was higher than anticipated. At 25°C , and at 5-10% levels, neither triethylamine, 1,4-diazabicyclo(2.2.2)octane (DABCO), nor 4-dimethyl-

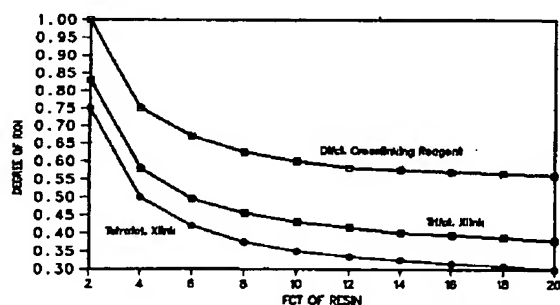


Figure 6—Degree of reaction at gel point (by Carothers equation)

Table 1—Basicity of Some Commercially Available Catalysts For the Michael Reaction

Base	Class	pK_b
Triethylamine (Et_3N)	amine	10.7
1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU)	amidine	12.5
1,5-Diazabicyclo(4.3.0)non-5-ene (DBN)	amidine	12.7
Tetramethylguanidine (TMG)	guanidine	13.6
Sodium hydroxide (NaOH)	hydroxide	~14

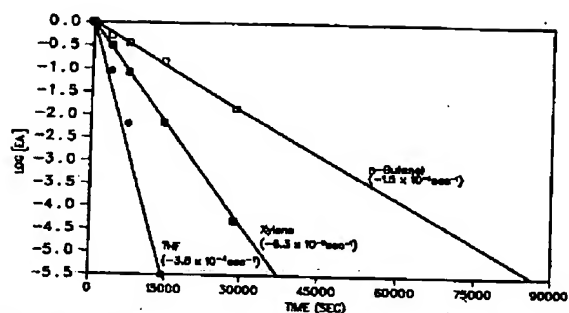


Figure 7—Michael reaction of the model system; TBAH catalyst (5 mol%); 25°C

aminopyridine (DMAP) would catalyze the Michael reaction; all of these compounds are basic catalysts of relatively low pK_b . As expected, the rate of the Michael reaction increased with increasing catalyst levels; with TMG, the correlation between the rate of reaction and the catalyst level (1-8 mole%) was nearly linear.

The relative amount of the bis-Michael adduct (4) which was produced varied considerably between the different types of catalysts. As discussed previously, formation of the bis-adduct would accelerate curing in an actual coatings system. If measured when half the ethyl acrylate was consumed, the amidine bases DBU and DBN provided bis/mono adduct ratios (4/3) of about 0.7, which was far higher than the bis/mono adduct ratio of 0.04 achieved with the hydroxide bases. TMG was closer to the amidines, with a bis/mono-adduct ratio of 0.3. Thus, at catalyst concentrations which provided equal rate constants, the amidine and guanidine catalysts would be predicted to provide more densely crosslinked systems than the hydroxide bases, partially at the expense of pot life.

The Michael reactions of isobutyl acetoacetate with several other activated olefins (Michael acceptors) were briefly examined to establish a general order of reactivity. Ethyl acrylate was clearly the most reactive olefin studied, but diethyl maleate also reacted readily. Methyl methacrylate (MMA) and ethyl crotonate were notably less reactive, while ethyl cinnamate barely participated in TMG-catalyzed Michael reactions at ambient temperatures.

PREPARATION OF THERMOSET MATERIALS—GEL POINT EXPERIMENTS

Our catalyst evaluation was extended to the preparation of thermoset materials, via the ambient temperature crosslinking of acetoacetylated acrylate, polyester, and cellulosic materials. This evaluation of Michael crosslinking technology occurred in two distinct technical phases. First, a series of gel time experiments was used to determine the general versatility of the Michael approach to crosslinking; the crosslinking of two acrylic, AAEM-based resins was then examined in greater detail.

CROSSLINKING ACETOACETYLATED RESINS

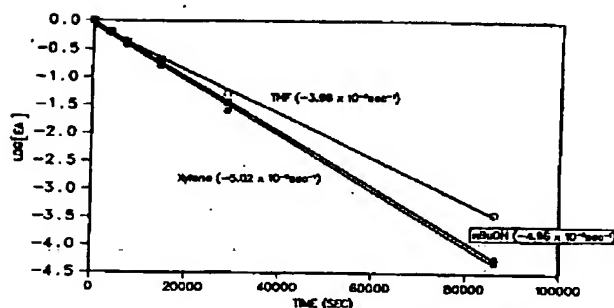


Figure 8—Michael reaction of the model system; TMG catalyst (5 mol%); 25°C

Two acetoacetylated acrylic resins were synthesized by the radical-promoted, solution polymerization of AAEM with MMA. The physical properties of these copolymers, containing 20 and 30 mol% AAEM, respectively, are summarized in Table 4. These resins had significantly reduced solution viscosities and glass transition temperatures when compared with MMA or MMA/hydroxyethylmethacrylate (HEMA) copolymers; this was an expected and desirable result of introducing bulky pendant groups onto the polymer backbone.

In the first of the aforementioned series of gel point experiments, our 20 mol% AAEM/MMA copolymer (fw 614/acetoacetyl group) and TMPTA were dissolved in 50/50 butanol/xylene to afford a solution (36% solids) which was 0.5 M in both acetoacetate and acrylate functionality. The addition of 2.5 mol% (relative to the acetoacetyl groups) TMG catalyst gelled this solution in six hours (Table 5); doubling this catalyst level to 5 mol% reduced the gel time by a factor of 3, to two hours. Gel times could be shortened by replacing the 5 mol% TMG (gel time = 6 hr) with a similar concentration of DBN (3 hr) or TBAH (4 hr), or lengthened with DBU (22 hr), which was consistent with predictions from our model study and mechanistic analysis. The gel time could be shortened by the addition of excess TMPTA; doubling the TMPTA concentration reduced the gel time by a factor of ~1.5.

Little dependence on the concentration of the acetoacetylated polymer was observed (in the 0.1-1 M range), and in several cases the more dilute samples gelled faster.

Application of the Carothers equation indicated that the number of functional (acetoacetyl) groups per polymer

Table 2—Pseudo-First-Order Rate Constants, Five Mole% Catalyst ($\times 10^3 \text{ sec}^{-1}$)

Catalyst	Solvent			
	THF	Xylene	nBuOH	EEP
KOH	29	insol.	20	—
nBu ₄ NOH	30	10.5	6.3	—
TMG	5.8	5.0	7.7	8.3
DBU	2.8	2.7	3.7	—
DBN	29	—	—	—
Et ₃ N	<0.1	—	—	—

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Table 3—Effect of Catalyst Concentration on the Rate of Michael Reactions
THF, 25°C

Catalyst	Concentration	Rate ($\times 10^3 \text{ sec}^{-1}$)
nBu ₄ NOH (TBAH)	5%	30
	2	4.6
TMG	10	21
	8	7
	5	5.8
	4	4.4
	2	1.0
DBU	5	2.8
	2	0.1
DBN	5	29
	2	2.7

molecule would also affect coatings cure, especially on materials with 2-20 functional groups. It was also anticipated that the concentration of both functional groups would become important as the acrylate groups became attached to the polymer and thus became less mobile; effective crosslinking would then depend on the physical proximity of functional groups. This dependency was observed by the comparison of a 10 mole% AAEM/MMA copolymer with the 20 mole% AAEM/MMA copolymer described previously; at identical concentrations of all functional groups, the less functionalized polymer required four times longer to gel (6 vs 24 hr). This result also established that our model system could be used to predict relative reactivities of different Michael systems and catalysts, but was not itself sufficient to predict cure times for different polymer systems.

The importance of functional group accessibility became even more apparent with acetoacetylated polyester resins and cellulosic polymers. These materials were prepared by acetoacetylating pendant hydroxyl groups on the polymers with diketene or methyl acetoacetate. In these polyesters and cellulose, the acetoacetyl groups were attached directly to the polymer backbone without the benefit of a spacer group as is present in AAEM, and this was reflected in slower cure rates under conditions similar to those used with the AAEM/MMA copolymers. Furthermore, the gel time of polymers with more hin-

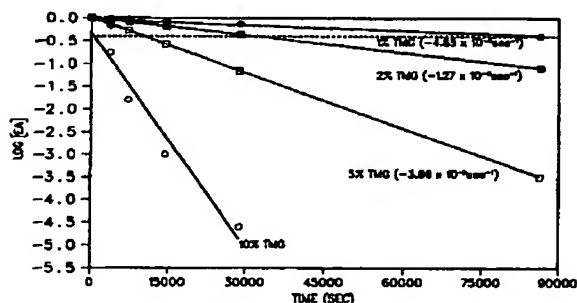
dered acetoacetyl groups appeared to decrease more rapidly with decreasing functional group concentrations than was the case with the AAEM based polymers. It was possible to offset the slower rates by increasing the concentrations of both functional groups via higher solids formulations. This approach was greatly simplified by the viscosity-reducing properties of the acetoacetyl group. Increasing the number of acetoacetyl groups per molecule was also found to enhance cure rates, especially with lower molecular weight species.

Cellulose triacetoacetate was readily crosslinked with TMPTA, while several less highly acetoacetylated cellulose esters (mw~12500/acetoacetyl group) could not be gelled. In an alternate approach to crosslinked cellulosic systems, TMG was used to catalyze the crosslinking of an acryloylated cellulosic with glycerol trisacetoacetate; crosslinking occurred, as demonstrated by sample gelation within one hour. This "reverse" approach to Michael-type crosslinking should be readily extended to make other coatings systems.

PREPARATION OF COATINGS BASED ON ACETOACETYLATED RESINS

The two AAEM/MMA copolymers which were previously discussed were selected for a more thorough examination. DBU was selected as the catalyst which would provide the greater cure latitude and the longer pot lives which were one of our initial objectives. Cure response curves (Figure 10) were determined for both resins, using a stoichiometric amount of TMPTA as the crosslinking reagent, at four different catalyst levels.

The response curves were determined by hourly viscosity measurements; that level of catalyst which would provide a pot life of greater than eight hours and still afford complete cure was sought. Consistent with earlier observations, the higher degree of functionality on the 30 mol% AAEM resin resulted in complete cure at markedly lower levels of catalyst. For the resin containing 20 mol% AAEM, 2 mol% of DBU (relative to the acetoacetyl groups) gave the desired pot life and also effected complete cure, while 1 mole% of DBU was sufficient to cure the resin which contained 30 mole% AAEM. These catalyst levels are quite low when viewed as a percentage of the total coatings formulation (0.07-0.11%), and were used for the remainder of the coatings evaluations. The

**Figure 9—Michael reaction of the model system; TMG catalyst; 25°C****Table 4—AAEM/MMA Copolymers and Properties**

	Resin (mol% AAEM)		
	0 mol% ^a	20 mol%	30 mol%
Wt% AAEM	0	34.9	47.8
M _n	9590	6970	7650
T _g (°C)	105	57	52
% Solids	59.0	57.7	58.0
Brookfield viscosity (cP $\times 10^3$)	471	42	24

^a MMA control.

specific formulations which were tested are described in Table 6. It should be noted that these resins were selected simply to provide a general indication of the potential of this technology, and were not formulated to enhance any particular properties.

The premixed ingredients were sprayed onto cold-rolled steel panels which had been pretreated with Bonderite® 37, and the coatings were then allowed to cure for seven days at ambient temperature. The performance properties of the resulting AAEM-based enamels were evaluated (Table 7) and found to have good overall coatings performance, particularly with respect to stain resistance. The major problem which was encountered was the relatively poor hydrolytic stability, as seen in Cleveland humidity tests. It was reasoned that the amidine base which remained in the coating would catalyze the hydrolysis of the crosslinked film. Indeed, a low temperature bake (100-120°C) improved the hydrolytic stability of the coating to the point that the coatings easily passed 500 hr of Cleveland humidity testing. A more volatile amidine catalyst, a catalyst neutralization scheme, or a catalyst less effective at ester hydrolysis may provide further enhancements in the technology of Michael-cross-linked coatings.

EXPERIMENTAL

Model System—Typical Procedure

A stock solution of isobutyl acetoacetate (7.9 g, 0.05 mol), ethyl acrylate (5.41 mL, 0.05 mol), and 0.5 g of p-dichlorobenzene (internal standard) was diluted to

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Table 5—Preparation of Thermoset Materials via the Michael Reaction

Resin	[AcAc] ^a	Catalyst	Conc. ^b	Solvent	Gel Time (hr)
Polyester ^c	.80M	KOH	1%	nBuOH/ xylene	1
"	"	TMG	5	"	1
"	"	TMG	2	"	17
"	"	TMG	1	"	no gel
"	"	DBU	5	"	1
CHDM (AcAc) ₂	.50M	TMG	10	"	6
10% AAEM/ MMA ^d	.27M	TMG	5	"	25
"	.21M	TMG	10	acetone	1
20% AAEM/ MMA	.25M	TMG	5	nBuOH/ xylene	6
"	"	TBAH	5	"	4
"	"	DBN	5	"	3
"	"	DBU	5	"	22
Cellulose (AcAc) ₃	.33M	TMG	5	acetone	2
"	.10M	TMG	5	"	1
Cellulose acrylate ^e	.25M	TMG	5	"	2
"	.20M	TMG	10	EEP	1

(a) Concentration of acetoacetyl (AcAc) groups in solution.

(b) Catalyst concentration in mol% relative to acetoacetyl groups.

(c) DMCD/NPG/TMP/IPA resin, Mw 6000, 400 OH group, 90% acetoacetylated.

(d) 10 mol% AAEM in monomer feed; see Experimental section.

(e) Cellulose acetate butyrate, acetylated with acryloyl chloride (mw 400/acryloyl group); crosslinked with glycerol triacetoacetate.

CROSSLINKING ACETOACETYLATED RESINS

50.00 mL with THF. A 10.00 mL volumetric flask was filled with a portion of this solution and immersed in a Haake constant temperature bath whose contents were maintained at $25.0 \pm 0.1^\circ\text{C}$. TMG (5 mole%, 0.063 mL) was added to the thermally equilibrated solution and the flask was agitated. Reaction aliquots (0.5 mL) were re-

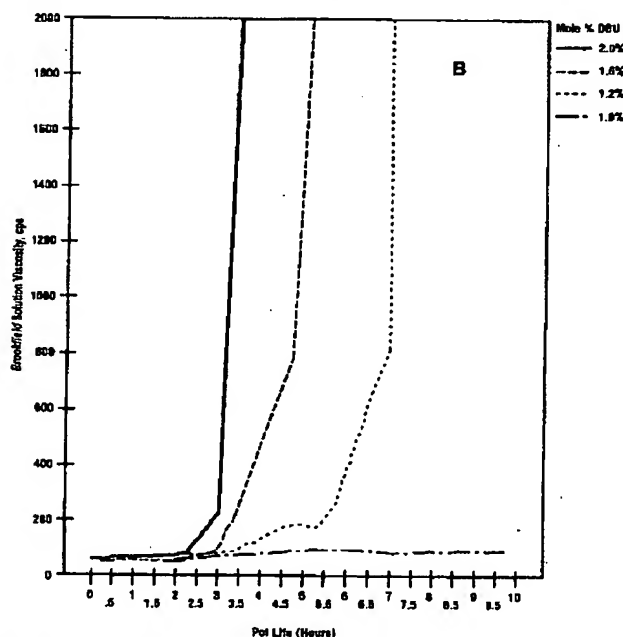
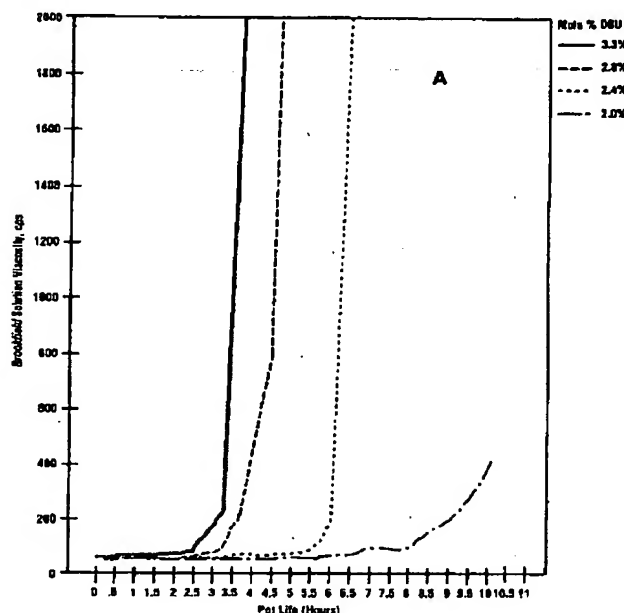


Figure 10—A: Michael addition, DBU catalyst, 20 mole% AAEM resin, pot life. B: Michael addition, DBU catalyst, 30 mole% AAEM resin, pot life

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moved at Time=0, and then at 30-60 min intervals for the next eight hours. These aliquots were added to a vial which contained 2.00 mL of diethyl ether and 0.200 mL of 0.1N HCl, and the vials were thoroughly shaken and the phases allowed to separate. A portion of the ethereal layer was transferred to a sample vial for GC analysis. Control experiments established that the extraction procedure completely quenched the Michael reaction and that the relative amounts of the reactants (except the catalyst), the products, and the internal standard were unchanged by the extraction procedure. The samples were then autoinjected (HP7673A) onto a 30 m DB-5 capillary column in an HP5890 gas chromatograph (injector 220°C; oven 70°C for 2 min, then +20°C/min to 240°C) equipped with a flame ionization detector. Each sample was injected twice, and the integrated values of the peak size versus the internal standard were averaged. The log [ethyl acrylate] was plotted as a function of time to calculate a pseudo-first-order rate constant in sec^{-1} . With those reactions which were fast enough to progress beyond pseudo-first-order behavior, the data obtained during the first half-life of ethyl acrylate was used to reflect the rate while the model was simulating coatings cure. All individual lines had regression coefficients (R^2) >0.970, but repeated runs of "identical" reactions suggested that the precision of any given measurement was ~20%.

Preparation of Acrylic Resins

A heated, four-necked round-bottomed flask with electronic temperature control was equipped with an air driven stirrer, a condenser, and an addition funnel. The resin formulation was calculated so as to provide a final product at 60% solids. The majority of the Ektapro® EEP solvent was charged into the nitrogen purged flask, and was then heated to 100°C. The monomers and Vazo® 67 initiator were dissolved in Ektapro EEP solvent, placed in the addition funnel, and added dropwise to the heated solvent over four hours. After the addition was complete, the reaction was maintained at 100°C for an additional half-hour; and additional ½ mole% of the initiator (as a

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Vazo is a registered trademark of E.I. duPont de Nemours & Co., Inc.

Table 6—Enamel Formulations Based on Michael-type Crosslinking

	Resin (Mole% AAEM)	
	20	30
Part A: Grind		
Resin (60 wt% in Ektapro EEP solvent)	43.6	32.6
Trimethylolpropane triacrylate	3.6	4.3
TiO ₂	20.4	15.2
MIAC	14.4	17.8
Ektapro EEP solvent	7.9	14.4
n-Butanol	7.9	14.4
Part B: Catalyst		
DBU (5 wt% in n-butanol)	2.2	1.3
	100.0	100.0
#4 Ford Cup viscosity, sec	30	32

90

Table 7—Properties of Enamel Formulations Based on Michael-type Crosslinking

	Resin (Mole% AAEM)	
	20	30
Average film thickness, mil	1.2	1.2
Gloss at 60°	83	82
at 20°	74	70
MEK rub resistance		
Number passed	250	250
Pencil hardness to mar	4H	3H
Impact resistance, in.-lbs		
Direct	8	18
Reverse	4	4
Stain resistance*		
Iodine after 5 min	N	N
Iodine after 30 min	N	VS
Ink after 24hr	N	N
Chemical resistance*		
Sulfuric acid after 1 hr	N	N
Sodium hydroxide after 1 hr	N	N

(*)Scale: N=no effect; and VS=very slight effect.

10 mol% solution in Ektapro EEP) was added to conclude the reaction. The solution of the polymer in Ektapro EEP was then cooled for storage.

Preparation of Thermoset Materials

An acetoacetylated polymer* and a stoichiometric quantity (based on individual functional groups) of TMPTA were dissolved in either EEP or 50/50 nBuOH/xylene at the specified concentration (typically 33% solids). Aliquots (10 mL) of these stock solutions were pipetted into 15 mL vials, a catalyst was added (typically 5 mole% relative to acetoacetyl groups), and the vials were repeatedly inverted until they gelled. A visible viscosity increase was generally noted only very shortly before the gel point.

SUMMARY AND CONCLUSIONS

A model system was developed to evaluate catalysts for the Michael reaction of acetoacetylated compounds and to learn more about the reaction process. This model was used to demonstrate that alkylated amidine (DBU, DBN) and guanidine (TMG) bases will catalyze the Michael reaction at ambient temperature, and that reaction rates can be controlled by the choice of the catalyst and the level at which it is used. This discovery provides an alternative to the more conventional hydroxide bases, although each class of catalysts has its own merits. The hydroxide bases are the low cost materials and are extremely reactive, but they suffer from lesser solubility in nonpolar solvents. Also, the hydroxide bases are often

Hydroxyl groups were acetoacetylated at 45°C, typically in ethyl acetate solution, with DMAP catalyst via the slow addition of diketene.

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used at very low levels, which increases the susceptibility of these systems to catalyst neutralization by acidic impurities. The advantages of the alkylated amidines and guanidines include their ready solubility, even in xylene, and the diversity provided by the wide variety of materials available within these compound classes.

We have demonstrated that amidine and guanidine catalysts will promote the ambient temperature crosslinking of acetoacetylated acrylate, polyester, and cellulosic polymers via the Michael reaction. In an extension of the Michael crosslinking technology, we crosslinked an acryloylated cellulosic polymer with a trisacetoacetate using TMG. Many acetoacetylated polymers and polyols are readily amenable to high solids application, and the Michael reaction is accelerated under these conditions; the catalyst must be carefully chosen to provide the best balance between cure rate and pot life.

Much remains to be learned about the Michael reaction, especially as it applies to the preparation of thermoset coatings. We hope that others will build on our efforts to understand this reaction and can develop practical coatings technology based on the Michael reaction of acetoacetylated monomers and polymers.

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